Influence of additives on the radiative properties of thermal carbon plasma during fullerene production

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Abstract: Influence of additives on the radiative properties of thermal carbon plasma during fullerene formation was studied in an RF plasma reactor. The C₂ Swan spectrum was prominent in most of the measured spectra. Features attributable to the C₃ radical were detected in some of the spectra. The vibration-rotation temperature of the Swan transitions of the C₂ radical in the plasma was determined using least-squares fitting to accurate theoretical spectra.

Keywords: RF plasma, fullerene, C₂, C₃, Swan band, Swan temperature

1. Introduction
Since their discovery a lot of research work has been reported on the fullerenes worldwide. Many papers have been published about the advantageous and disadvantageous effects of some additives on fullerene formation. However, only a few studies were reported for fullerene synthesis in RF plasma reactor.

It is known from thermodynamic calculations that most of carbon vapor at temperature of 2000 K, or at higher ones contains C₃ in high concentration [1]. The formation temperature for fullerenes ranges from 2250 to 3800 K. This temperature range also corresponds to the highest concentration of the C₂ and C₃ species, which are considered as fullerene precursors [2]. But there are still many open questions concerning the synthesis processes leading to large carbon structures.

Optical emission spectroscopy (OES) is a useful method for monitoring the plasmas. With OES method chemical species in the plasma can be identified, and various parameters such as temperatures can be determined without any influences on the plasma state. The C₂ radical is widely used as a diagnostic tool for carbon plasmas.

The C₃ molecule is one of the most studied triatomic molecules in the spectroscopy. In high-temperature sources, such as equilibrium carbon vapors, flames, and carbon plasmas a spectral continuum was observed at 400 nm. The molecular 400 nm continuum consists of a great number of individual transition lines. Therefore, it is commonly referred to as pseudo continuum or line continuum to emphasize that it arises from bound-bound transitions but not from free-free or free-bound continuum transitions. The first detailed vibrational-electronic (vibronic) analysis of the 4050Å laboratory spectrum was published in 1963 [3].

There are in principle several vibronic bands of C₃ that could be observed, but the detection of C₃ in carbon plasma emission spectra is practically limited to the observation of the Swings bands centered at 405 nm, A¹Π_g-X¹Σ_g. Between many spectroscopic investigations of C₃ molecule, there are no spectroscopic studies for C₃ molecule during fullerene formation in RF thermal plasma.

In this work spectroscopic measurements were carried out during fullerene synthesis in RF thermal plasma in presence of different additives. We studied the effect of additives on the emitted spectra and identified the atomic lines and molecular bands. From the intensities the excitation and vibration-rotation temperatures were determined.

2. Experimental
Pure graphite powder (KS4, Timcal Co., D₅₀=2.8 µm) and its mixtures with various additives, such as Fe (D₅₀: 35 µm), Si (D₅₀: 14.9 µm) and B (D₅₀: 28.2 µm) powders were subjected to thermal plasma treatment in a RF plasma system (3-5 MHz, TEKNA PL-35 torch). A copper containing waste graphite powder (D₅₀: 37.3 µm) was used as precursor for the fullerene synthesis, as well. Effect of nitrogen in the plasma gas was also investigated.

In the experiments, the main product was solid soot collected from the water cooled reactor wall.

In all runs the gas flow rates and the plate power were set to values as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma gas (slpm)</td>
<td>8 Ar + 8.5 He</td>
</tr>
<tr>
<td>Sheath gas (slpm)</td>
<td>12 Ar + 28 He</td>
</tr>
<tr>
<td>Carrier gas (slpm)</td>
<td>6 He</td>
</tr>
<tr>
<td>Plate power (kW)</td>
<td>28</td>
</tr>
</tbody>
</table>

The experimental parameters are collected in Table 1.

For more detailed data we refer to a previous paper [4]. Fullerenes were extracted with toluene from the resulting soot. Amount of fullerenes was measured by UV-VIS spectrophotometer, while their composition was measured by HPLC technique.
<table>
<thead>
<tr>
<th>Run</th>
<th>Additive (wt%)</th>
<th>Feed rate (g·h)</th>
<th>$E_{spec}$ (kWh·g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>19</td>
<td>1.47</td>
</tr>
<tr>
<td>2</td>
<td>N$_2$</td>
<td>22</td>
<td>1.27</td>
</tr>
<tr>
<td>3</td>
<td>Fe (5)</td>
<td>13</td>
<td>2.15</td>
</tr>
<tr>
<td>4</td>
<td>Fe (5)</td>
<td>46</td>
<td>0.61</td>
</tr>
<tr>
<td>5</td>
<td>Fe (20)</td>
<td>17</td>
<td>1.65</td>
</tr>
<tr>
<td>6</td>
<td>Si (5)</td>
<td>33</td>
<td>0.85</td>
</tr>
<tr>
<td>7</td>
<td>B (5)</td>
<td>12</td>
<td>2.33</td>
</tr>
<tr>
<td>8</td>
<td>Cu (5)</td>
<td>44</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Table 1: Experimental parameters

Emissions of plasma were detected perpendicularly to the axis of plasma flame through a quartz glass window at 10 cm distance from the bottom of plasma nozzle. The wavelength was selected by a 55 cm focal length monochromator (TRIAX 550 Jobin-Yvon). Gratings with 300, 1200 and 1800 grooves/mm were used. Light was collected and transferred to the entrance slit by a multi-legged fiber optics. Plasma emission was detected by an optical multi-channel analyzer (CCD-3000). The spectral range available was 200-1000 nm.

3. Results and discussion

The spectra of carbon plasmas consisted of atomic lines and molecular bands, depending on the additives. One of the most prominent bands in the optical emission spectra was the C$_2$ Swan system.

Emission spectrum of the plasma in the presence of graphite/iron mixture contained many atomic lines of iron. Some of these atomic lines are overlapping with the C$_2$ Swan band (Fig. 1). The lines in the range between 700-800 nm are well known spectral features originating from Ar atoms.

In presence of nitrogen added to plasma gas molecular bands of CN radicals were also detected in the spectra. Strong features for the CN violet band centering at 388 nm are seen in Fig. 2.

![Fig. 2 Emission spectrum of RF thermal carbon plasma in the presence of nitrogen](image)

In some spectra, near 400 nm, the so called pseudo-continua of C$_3$ band could also be observed.

![Fig. 3 A possible spectroscopic signature of C$_3$ Swings transitions of carbon plasma](image)

The most intense sign of the C$_3$ Swings band was observed without any additive (Fig.3), while in cases of N, B and Si additives it could not be detected. A weak feature of a 400 nm continuum could be observed in spectra’s taken in presence of 5 wt% Fe and Cu. However, in the presence of 20 wt% Fe the continuum could not be observed. Some of the iron atomic lines are overlapping with the C$_3$ Swings band as it can be seen in Figure 4.
Our previous experiments of fullerene synthesis showed that in most cases the extractable fullerene content of the soot can be related to the extent of evaporation. It supports the importance of the C\textsubscript{2} concentration in the reactor [4, 8]. The C\textsubscript{2} Swan temperatures were determined by a least-squares fitting program NMT applying the Nelder-Mead algorithm, developed at the University of Tennessee Space Institute [5-7]. The procedure is based on calculating the positions and the intensity of the transitions using an accurate quantum mechanical approach. C\textsubscript{2} Swan temperatures were determined during fullerene productions in presence of different additives. The highest Swan vibration-rotation temperature 6100 K was evaluated for the case when no additive was applied.

In the presence of additives a decrease of vib-rot temperatures was observed. In presence of N, Si, Fe and Cu additives the resulted vibrational-rotational temperatures are between 3800-4100 K, till in presence of B their value is 4500 K.

The same fitting program can be used for the CN violet band. Comparison of C\textsubscript{2} Swan and CN band temperatures were made in the same spectra. These temperatures showed a difference less then 200 K. The error in the vibrational-rotational temperatures reported here are about ±200 K. The standard deviations of relative intensity of the fit in most cases were below 0.4 in our work.

In carbon plasmas without additives the lower values of rotational temperatures of C\textsubscript{2} radical (nearly 3000 K) were good indicators of higher fullerene yield [8]. In presence of Fe additive lower C\textsubscript{2} vib-rot temperature and higher fullerene yield was reached than in the absence of additive. In presence of other additives the decrease of C\textsubscript{2} vib-rot temperature didn’t result in higher fullerene yield. In these cases other effects seem to play role in fullerene formation.

The excitation temperature (T\textsubscript{ex}) was determined by the Boltzmann plot according to the following equation:

\[
\log(I_{ij}/g_i f_{ij}) = -E_i/kT_{ex} + C \quad (C: \text{constant})
\]

where \(I_{ij}\) is intensity of emission, \(\lambda_{ij}\) is wavelength of each peak, \(g_i\) is statistical weight of upper \(i\) energy level, and \(f_{ij}\) is oscillator strength. \(E_i\) is excitation of upper \(i\) energy level, and \(k\) is Boltzmann constant. The \(\lambda_{ij}, g_i, f_{ij}\) and \(E_i\) values were taken from the literature [9].

The emission spectrum of the pure Ar plasma consisted of mainly Ar I lines with only some Ar II emissions of low intensity. The excitation temperature was determined using Ar I spectral lines observed in the region of 650-1000 nm. These spectral lines are not overlapping with molecular bands. C. Wang and coworkers determined the excitation temperatures of plasma using 703 nm and 714 nm Ar I spectra lines [10]. We employed for our T\textsubscript{ex} determination the same two spectral lines. Excitation temperature of pure Ar plasma was found to be 9000 K. The result was in good agreement with data published by some authors [11]. They have determined the electron temperature of the Ar plasma by the line to continuum method, and found it to be 10000 K. The Ar excitation temperature in carbon plasma with no additive was 7800 K. In presence of Si and Fe additives Ar excitation temperature was 6900 K, while in presence of nitrogen this value was 8900 K and in presence of B was 10000 K.

The differences between excitation temperatures and Swan temperatures imply differences of special distributions of excited chemical species.[12].

<table>
<thead>
<tr>
<th>Additive (wt%)</th>
<th>C\textsubscript{2} Swan temp. (K)</th>
<th>Excit. temp. (K)</th>
<th>Yield (% wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>6100</td>
<td>7800</td>
<td>4.92</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>3800</td>
<td>8900</td>
<td>1.27</td>
</tr>
<tr>
<td>Fe(20)</td>
<td>4100</td>
<td>6900</td>
<td>6.10</td>
</tr>
<tr>
<td>Si(5)</td>
<td>3900</td>
<td>6900</td>
<td>3.36</td>
</tr>
<tr>
<td>B(5)</td>
<td>4500</td>
<td>10000</td>
<td>1.18</td>
</tr>
</tbody>
</table>
The highest fullerene content was obtained with 20 wt% iron. Mixing of a small amount of nitrogen to the plasma gases resulted in very low fullerene content compared to the other additives.

With Si, B and Cu addition, less fullerene could be synthesized than with pure graphite powder (KS4). Effect of additives on the fullerene composition was studied by HPLC measurements. Chromatograms of the extracts and assignment of the peaks are shown in Fig. 6. Due to its high UV absorption $C_{60}$ was detected at 525 nm, while the other fullerenes were measured at 330 nm.

Fullerene compositions of the samples were compared by the calculation of normalized HPLC peak areas measured at 330 nm. Thus, it resulted in data for $C_{70}$ and higher fullerenes.

![HPLC results of toluene extracts. Assignation of peaks: 1: $C_{60}$, 2: $C_{60}$O, 3: $C_{60}$O$_2$, 4: $C_{70}$, 5: $C_{70}$O, 6: $C_{70}$, 7: $C_{78}$, 8: $C_{82}$, 9: $C_{84}$, 10: $C_{86}$.](image)

Fig. 6 HPLC results of toluene extracts. Assignation of peaks: 1: $C_{60}$, 2: $C_{60}$O, 3: $C_{60}$O$_2$, 4: $C_{70}$, 5: $C_{70}$O, 6: $C_{70}$, 7: $C_{78}$, 8: $C_{82}$, 9: $C_{84}$, 10: $C_{86}$.

Fullerene compositions were similar in almost all cases, excepting the conditions in the presence of boron. In this case the peak areas corresponding to $C_{82}$ and $C_{84}$ were much higher, than in other samples. To emphasize differences in composition, the relative peak areas of $C_{70}$ (in the range of 58-74%) were not shown in the Fig. 6.

**4. Conclusions**

RF carbon plasma flames with additives were analyzed by emission spectroscopy during fullerene formation.

In the region of 350-1000 nm, near $C_2$ different atomic lines in function of the additive used, $C_2$ and $C_3$ optical emission spectra were observed. Feature of a 400 nm continuum attributed to $C_3$ molecule could be observed in spectra taken in presence of 5 wt% Fe and Cu, while in cases of N, B and Si additives it could not be detected. The most intense sign of the $C_3$ Swings band was observed without additives.

$C_2$ Swan temperatures were determined during fullerene productions in presence of different additives. The vibrational-rotational temperatures were found between 3800-6100 K. In the presence of additives a decrease of these temperatures was observed. In presence of Fe additive lower $C_2$ vib-rot temperature and higher fullerene yield was reached than without additives. Excitation temperature ($T_{ex}$) was determined by the Boltzmann plot method. The excitation temperature of pure Ar plasma was found to be 9000 K. The Ar excitation temperature in carbon plasma with no additive was 7800 K. In presence of Si and Fe additives, the Ar excitation temperature was found to be 6900 K. Higher excitation temperatures like 8900 K were obtained in presence of N$_2$, till in presence of B these values were 10000 K.

From these experiments no obvious correlations were found between Ar excitation, $C_2$ vib-rot temperatures, and fullerene yield.

**References**

[9] NIST Atomic Database